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L'Hopital's Rule in Chemistry: Irreversible Morphing into Reversible Isothermal Expansions

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L'Hôpital's Rule in Chemistry; Irreversible Morphing into Reversible Isothermal Expansions

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I. SYNOPSIS

L'Hôpital's Rule is discussed in the case of a reversible isothermal expansion, with the idea of reinforcing ideas from elementary calculus. We investigate the transition from irreversible to reversible expansions in two ways, with the more sophisticated method yielding a gorgeous example of limit taking employing you know who's rule.

II. INTRODUCTION

To construct a reversible work path in which we will pass to the limit of an infinite number of irreversible paths appended together, we use an example of isothermal irreversible work, as illustrated in Figure 1. The four constant pressure expansions (against changing static pressures) are carried out irreversibly. The total work is the sum of the work associated with each of the four constant pressure steps, each chosen (in our example) to have one fourth of the pressure drop assigned in going from the initial to the final pressure.

We then have

$$\begin{aligned} w_{irrev} =& \\ +p_2(V_2 - V_{initial})& \\ +p_3(V_3 - V_2)& \\ +p_4(V_4 - V_3)& \\ +p_{final}(V_{final} - V_4)& \end{aligned} \tag{2.1}$$

which becomes

$$\begin{aligned} w_{irrev} =& \\ +p_2\left(\frac{nRT}{p_2} - \frac{nRT}{p_{initial}}\right)& \\ +p_3\left(\frac{nRT}{p_3} - \frac{nRT}{p_2}\right)& \\ +p_4\left(\frac{nRT}{p_4} - \frac{nRT}{p_3}\right)& \\ +p_{final}\left(\frac{nRT}{p_{final}} - \frac{nRT}{p_4}\right)& \end{aligned} \tag{2.2}$$

or

$$\begin{aligned} w_{irrev} =& \\ +nRT\Bigg[p_2\left(\frac{1}{p_2} - \frac{1}{p_{initial}}\right)& \\ +p_3\left(\frac{1}{p_3} - \frac{1}{p_2}\right)& \\ +p_4\left(\frac{1}{p_4} - \frac{1}{p_3}\right)& \\ +p_{final}\left(\frac{1}{p_{final}} - \frac{1}{p_4}\right)\Bigg]& \end{aligned} \tag{2.3}$$

or

$$\begin{aligned} w_{irrev} =& \\ +nRT\Bigg[\left(\frac{p_{initial} - p_2}{p_{initial}}\right)& \\ +\left(\frac{p_2 - p_3}{p_2}\right)& \\ +\left(\frac{p_3 - p_4}{p_3}\right)& \\ +\left(\frac{p_4 - p_{final}}{p_4}\right)\Bigg]& \end{aligned} \tag{2.4}$$

or

$$\begin{aligned} w_{irrev} = -nRT\Bigg[&\left(\frac{\Delta p}{p_{initial}}\right) + \left(\frac{\Delta p}{p_2}\right) \\ &+ \left(\frac{\Delta p}{p_3}\right) + \left(\frac{\Delta p}{p_4}\right)\Bigg] \end{aligned}$$

Therefore, the total work is

$$w_{irrev} = -nRT\sum_{i=1}^{i=4}\frac{\Delta p}{p_i} \tag{2.5}$$

III. THE QUESTION

A. Traditional Conversion from Sum to Integral

We start with the last expression (Equation 2.5) and notice that as the upper limit of the summation is in-

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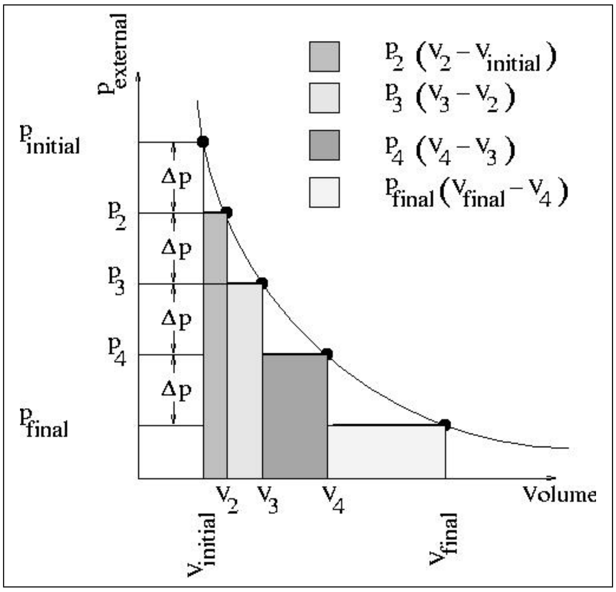

FIG. 1: Isothermal irreversible work

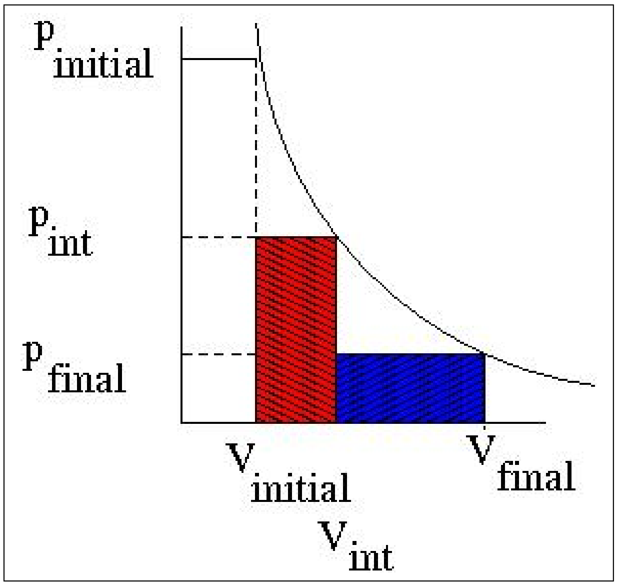

FIG. 2: One Intermediate step irreversible work

creased, one can write

$$w_{irrev} \to w_{rev} = -nRT \left(\sum_{i=1}^{i=large} \to \int_{p_{initial}}^{p_{final}} \right) \frac{\cancelto{dp}{\Delta p}}{p}$$

i.e.,

$$w_{rev} = -nRT \int_{p_{initial}}^{p_{final}} \frac{dp}{p}$$

B. L'Hôpital's Rule's Precursor Discussion

As an alternative to equal spacing of the various levels of pressure as we break up the work into smaller and smaller pieces, we can ask for the optimal choices of pressure which would make the irreversible work closest to what would eventually become the reversible (minimum) work. To do this, let's assume as a start that there's only one intermediate step (later there will be two and then three, etc.). Then the irreversible work (with one intermediate stage, see Figure 2) would be

$$w_{1/2} = -p_{int} \left(V_{int} - V_{initial} \right)$$

while

$$w_{2/2} = -p_{final} \left(V_{final} - V_{int} \right)$$

where the two compressions sequentially applied, take us from $p_{initial}$ to p_{final}.

$$w_2 = -p_{int} \left(\frac{nRT}{p_{int}} - \frac{nRT}{p_{initial}} \right) - p_{final} \left(\frac{nRT}{p_{final}} - \frac{nRT}{p_{int}} \right)$$

which can be re-written as

$$w_2 = -nRT \left(p_{int} \left(\frac{1}{p_{int}} - \frac{1}{p_{initial}} \right) + p_{final} \left(\frac{1}{p_{final}} - \frac{1}{p_{int}} \right) \right)$$

or

$$w_2 = -nRT \left(\left(1 - \frac{p_{int}}{p_{initial}} \right) + \left(1 - \frac{p_{final}}{p_{int}} \right) \right)$$

What we don't know is, what's the optimal choice of the intermediate pressure p_{int} (the notation will become obvious soon)? Let's take the derivative of w_2 with respect to p_{int} and set it equal to zero, looking for an extremum. We obtain

$$\frac{\partial w_2}{\partial p_{int}} = nRT \frac{\partial \left(\frac{p_{int}}{p_{initial}} + \frac{p_{final}}{p_{int}} \right)}{\partial p_{int}} \to 0$$

We obtain

$$\frac{p_{final}}{p_{initial}} = p_{int}^2$$

or

$$p_{int} = \sqrt{p_{final} p_{initial}} = \left(p_{final} p_{initial} \right)^{1/2}$$

which we write in the final form for reasons which will become clear. Now

$$w_2 = -nRT\left(\left(1-\frac{(p_{final}p_{initial})^{1/2}}{p_{initial}}\right)+\left(1-\frac{p_{final}}{(p_{final}p_{initial})^{1/2}}\right)\right)$$

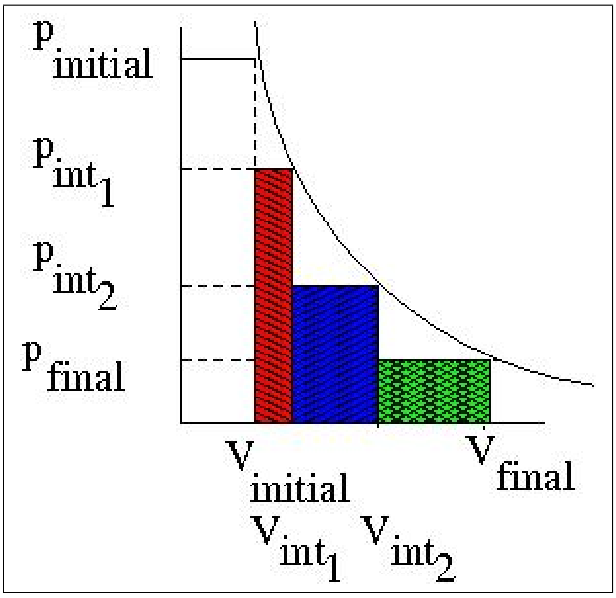

FIG. 3: Two Intermediate steps irreversible work

and this becomes

$$w_2 = -nRT\left(\left(1-\left(\frac{p_{final}}{p_{initial}}\right)^{1/2}\right)+\left(1-\left(\frac{p_{final}}{p_{initial}}\right)^{1/2}\right)\right)$$

which we re-write one more time (I promise, this is it!):

$$w_2 = -nRT2\left(1-\left(\frac{p_{final}}{p_{initial}}\right)^{1/2}\right)$$

If you glance below to Equation 4.1 you will see where we're going.

Let's do a two-step irreversible expansion now. We can see in Figure 3 that we have for the work

$$w_{1/3} = -p_{int_1}\left(V_{int_1}-V_{initial}\right)$$

while

$$w_{2/3} = -p_{int_2}\left(V_{int_2}-V_{int_1}\right)$$

$$w_{3/3} = -p_{final}\left(V_{final}-V_{int_2}\right)$$

where the three compressions sequentially applied, take us from $p_{initial}$ to p_{final}.

$$w_3 = -p_{int_1}\left(\frac{nRT}{p_{int_1}}-\frac{nRT}{p_{initial}}\right)-p_{int_2}\left(\frac{nRT}{p_{int_2}}-\frac{nRT}{p_{int_1}}\right)-p_{final}\left(\frac{nRT}{p_{final}}-\frac{nRT}{p_{int_2}}\right)$$

We now have

$$\frac{w_3}{nRT} = -\left(1-\frac{p_{int_1}}{p_{initial}}\right)-\left(1-\frac{p_{int_2}}{p_{int_1}}\right)-\left(1-\frac{p_{final}}{p_{int_2}}\right) \tag{3.1}$$

which is set up to take the partial derivatives with respect to p_{int_1} and p_{int_2} and separately set them equal to zero.

$$\left(\frac{\partial w_3}{p_{int_1}}\right)_{p_{int_2}} = -\frac{1}{p_{initial}}+\frac{p_{int_2}}{p^2_{int_1}} \to 0$$

$$\left(\frac{\partial w_3}{p_{int_2}}\right)_{p_{int_1}} = -\frac{1}{p_{int_1}}+\frac{p_{final}}{p^2_{int_2}} \to 0$$

From these we obtain

$$\frac{p_{int_1}}{p_{initial}} = \frac{p_{int_2}}{p_{int_1}}$$

and

$$\frac{p_{int_2}}{p_{int_1}} = \frac{p_{final}}{p_{int_2}}$$

Substituting these last two equations into Equation 3.1 results in

$$\frac{w_3}{nRT} = -\left(1 - \cancel{\frac{p_{int_1}}{p_{initial}}}\right)^{\frac{p_{int_2}}{p_{int_1}}} - \left(1 - \frac{p_{int_2}}{p_{int_1}}\right) - \left(1 - \cancel{\frac{p_{final}}{p_{int_2}}}\right)^{\frac{p_{int_2}}{p_{int_1}}} \tag{3.2}$$

Also, from these two equations we have

$$\frac{p_{final}}{p_{int_2}} \frac{p_{int_1}}{p_{initial}} = \frac{p_{int_2}}{p_{int_1}} \frac{p_{int_2}}{p_{int_1}}$$

i.e.,

$$\frac{p_{final}}{p_{initial}} = \left(\frac{p_{int_2}}{p_{int_1}}\right)^3$$

which allows us to write

$$\frac{w_3}{nRT} = -3\left(1 - \left(\frac{p_{final}}{p_{initial}}\right)^{\frac{1}{3}}\right) \tag{3.3}$$

Clearly, the generalization of this to more and more steps (there were three here) leads to Equation 4.1.

IV. L'HÔPITAL'S RULE EVALUATING THE REVERSIBLE WORK

What is the limit of w in the expression

$$w = -nRTm\left(1 - \left(\frac{p_f}{p_i}\right)^{1/m}\right) \tag{4.1}$$

Since L'Hôpital's Rule is taught almost exclusively in the form of a ratio, we recast the above in that form, ignoring the prefixed constant for the time being and obtaining:

$$ratio = \frac{\left(1 - \left(\frac{p_f}{p_i}\right)^{1/m}\right)}{\frac{1}{m}}$$

Now, we have the task according to L'Hôpital to take the derivatives of the numerator and denominator of this ratio (with respect to m), i.e., for the future numerator we have:

$$numerator = \frac{\partial\left(1 - \left(\frac{p_f}{p_i}\right)^{1/m}\right)}{\partial m}$$

We re-write this as

$$numerator = -\frac{\partial e^{\ell n\left(\frac{p_f}{p_i}\right)^{\frac{1}{m}}}}{\partial m}$$

and again:

$$numerator = -\frac{\partial e^{\frac{1}{m}\ell n\left(\frac{p_f}{p_i}\right)}}{\partial m}$$

which is

$$numerator = -e^{\frac{1}{m}\ell n\left(\frac{p_f}{p_i}\right)} \ell n\left(\frac{p_f}{p_i}\right) \frac{\partial\left(\frac{1}{m}\right)}{\partial m}$$

and one more time (into the fray):

$$numerator = +e^{\frac{1}{m}\ell n\left(\frac{p_f}{p_i}\right)} \ell n\left(\frac{p_f}{p_i}\right)\left(\frac{1}{m^2}\right)$$

The emergent denominator becomes

$$denominator = \frac{\partial\left(\frac{1}{m}\right)}{\partial m}$$

which is elementary, yields

$$denominator = -\frac{1}{m^2}$$

so the ratio we seek has the form

$$ratio = \frac{e^{\frac{1}{m}\ell n\left(\frac{p_f}{p_i}\right)} \ell n\left(\frac{p_f}{p_i}\right) \cancel{\frac{1}{m^2}}}{-\cancel{\frac{1}{m^2}}}$$

In the limit that $m \to \infty$, the final result becomes

$$-nRT\ell n\left(\frac{p_f}{p_i}\right)$$

A significantly better derivation of these results can be found in the literature, specifically, B. D. Joshi, *J. Chem. Ed.*,**63**, 24 (1986). Joshi goes even further than we, showing that the work is minimal, not just extremal.